

Study on temperature-enabling dynamics liquid chromatography and its application in uranium isotopes separation*

Yu-Jie Fu,^{1,2} Tao Yu,^{1,2,†} and Yu-Xiang Li^{1,2}

¹*Jiangxi Engineering Province Engineering Research Center of New Energy Technology and Equipment, East China University of Technology, Nanchang 330013, Jiangxi, China*

²*School of Nuclear Science and Engineering, East China University of Technology, Nanchang 330013, China*

Separation of uranium isotopes is not only a difficult scientific project, but also an engineering problem. A temperature-enabling dynamics liquid chromatography was designed for uranium isotopes separation based on dynamics liquid chromatography and liquid membrane diffusion model. This work prepared 'organic' and 'inorganic' chromatography columns filled ABS pellets and SiO₂ pellets, respectively. In order to improve the efficiency of separation, the injection-outflow self-control system and temperature-enabling cells were equipped to chromatography columns. The organic column optimal working conditions obtained by experiments were pH=2, enabling temperature=70°C and injection flow rate=15mL/min. Meanwhile, multi-stage separation experiment verified feasibility of uranium isotopes using organic column, the separation factor can reach 1.0184 and needed over 79 stages to enrich ²³⁵U abundance to 3%. The optimal conditions for inorganic column, determined through prior experiments, were pH=2, enabling temperature=50°C and injection flow rate=15mL/min. Multi-stage separation experiments using inorganic columns achieved a separation factor of 1.0110, requiring over 112 stages to enrich ²³⁵U abundance to 3%. Moreover, a series of mechanism experiments illustrated the mechanism of chromatography and confirmed liquid membrane and silica hydroxyl groups involvement in separation process. These studies identified the temperature-enabling dynamics liquid chromatography can effectively separate ²³⁵U from ²³⁸U, which provided a new research idea in the field of chromatography and isotope separation.

Keywords: Uranium isotopes separation; Dynamics chromatography; Temperature enabling; Maximum front enrichment value; Separation factor

I. INTRODUCTION

2 Nuclear energy is one of the most important means of solving the energy shortage in the world today. Nuclear power 3 plants use enriched uranium as fuel and utilize the enormous 4 energy released by the nuclear fission reaction to generate 5 electricity, which is a good solution to the problem of electric- 6 city consumption in many regions. However, the abundance 7 of ²³⁵U in nuclear fuel must be enriched to more than 3% 8 before it can be used by nuclear power plants. Therefore, 9 the separation and enrichment of uranium isotopes are essen- 10 tial in the production of nuclear fuel. Uranium, the heaviest 11 element in nature, has a mass difference of only 1% be- 12 tween ²³⁵U and ²³⁸U, which makes the separation of uranium 13 isotopes difficult. Historically, researchers have developed 14 several methods for separating uranium isotopes, including 15 gas diffusion, gas centrifugation, nozzle methods, laser en- 16 richment, chemical separation, electromagnetic separation of 17 isotopes, plasma separation[1–3], etc. The gaseous diffu- 18 sion method was the first historically developed and applied 19 method, but it has been phased out due to its lower separation 20

21 factor, larger plant size, and higher power consumption and 22 cost. Its separation factor is 1.0043 [4, 5]. Gas centrifugation 23 has the smallest energy consumption ratio in the world and 24 is the only method that can still be industrially produced, 25 its separation factor can reach 1.01. But this method 26 requires greater than 2000 separation stages, inconvenient and 27 polluting operations [6, 7]. The chemical methods include 28 chromatographic and extraction were created by Japan and 29 France, respectively. The chromatographic method named 30 Asahi Chemical Enrichment Process (ACEP), which used 31 isotope exchange chromatography for uranium enrichment. 32 ACEP employed a chromatography filled with a unique 33 anion exchange resin. When uranyl ions passed through the 34 column, they were adsorbed at the front end of the resin 35 layer, where isotope exchange reactions occur. Finally, a 36 reducing agent was used to elute the ions. The ACEP method 37 achieved a separation factor of 1.003. Since depleted solution 38 can be recirculated back into the column, the process did 39 not require large-scale cascade device[8, 9].The extraction 40 method, called Chemical Exchange (CHEMEX), relied on 41 isotope exchange reactions, separating uranium by exploiting 42 differences in isotopic behavior between two immiscible 43 liquid phases. CHEMEX achieves a separation factor of 44 approximately 1.0015, which was relatively low, requiring 45 thousands of stages to reach industrial-level enrichment. Both 46 processes have gradually been replaced by more efficient 47 methods, such as gas centrifugation, due to high energy 48 consumption and complex equipment[10, 11]. Laser method 49 exploits differences in spectral property between ²³⁵U and 50 ²³⁸U. Using uranium as ingredient, a laser with specific 51 frequency ionizes ²³⁵U into ²³⁵U⁶⁺, which were then collected 52 to achieve separation. The method has an extremely high

* Supported by the the Natural Science Foundation of Jiangxi Province, China (No. 20242BAB25153), the Opening Project of Jiangxi Engineering Province Engineering Research Center of New Energy Technology and Equipment (JXNE2022-07) and the Opening Project of the Jiangxi Province Key Laboratory of Polymer Micro/Nano Manufacturing and Devices (No. PMND202101).

† Corresponding author, Tao Yu, East China University of Technology, No. 418, Guanglan Avenue, Xinjian District, Nanchang City, Jiangxi Province, China, 13397097575, tyu@ecut.edu.cn

53 separation factor and requires very few separation stages.
 54 However, it is costly, involves complex technology, and
 55 demands harsh working conditions[12]. Uranium isotope
 56 separation technology has been stagnant for many years, so a
 57 new uranium enrichment scheme which is safe, efficient, en-
 58 vironmentally friendly, can be produced industrially and has
 59 low separation power is still needed[13, 14].

60 Since the beginning of the 20th century, chromatography
 61 has developed continuously and become an important means
 62 of separation and analysis, which has been used in many fields
 63 such as organic, analytical, chemical, medical, biochemical
 64 and environmental protection. Simultaneously, dynamics liq-
 65 uid chromatography is a major branch of chromatography and
 66 has been used as a highly efficient means of separating nat-
 67 ural macromolecules[15, 16]. Dynamics liquid chromatogra-
 68 phy is divided into two major categories, hydrodynamic chro-
 69 matography(HDC) and slalom chromatography(SC), both of
 70 which rely on the phenomenon of fluid dynamics within the
 71 chromatography to separate the solutes and generally do not
 72 involve chemical reactions[17–20].

73 In this paper, two types of dynamics liquid chromatog-
 74 raphy columns were fabricated for U isotopes separation,
 75 which were filled with ABS(Acrylonitrile-butadiene-styrene
 76 copolymer, A: acrylonitrile, B: butadiene, S: styrene ethenyl-
 77 benzene) plastic and SiO₂, respectively. Subsequently, a sys-
 78 tem of separation devices was constructed to cooperate with
 79 the column for automatic separation and collection. In the ex-
 80 periments, temperature-enabling method was used to improve
 81 the separation efficiency of uranium isotopes, and the separa-
 82 tion factor of uranium isotopes was obtained by multistage
 83 separation experiment. The most important innovation of
 84 this manuscript is the pulse chromatography method, which
 85 is to use the principle of chromatography to make the light
 86 and low valence substances in the solution at the front end
 87 of the column, and the heavy and high valence substances
 88 at the back end of the column, and then the light and
 89 heavy substances are separated by diverting. Through pulse
 90 injection, this separation can be carried out one by one, and
 91 each pulse is a separation process. Meanwhile, the effects of
 92 liquid membrane and functional groups on the experimental
 93 results were discussed to reveal the separation mechanism of
 94 the chromatographic column.

II. THEORY

96 2.1 Liquid membrane tidal diffusion model

97 Horvath and Lin (1978) proposed that a stagnant layer of
 98 nearly stationary mobile phase formed on filling surfaces in
 99 liquid chromatography, facilitating substance to transfer and
 100 exchange[21]. Previous studies indicated adsorption volumes
 101 often exhibited sharp turns and minor fluctuations over time
 102 (Supplementary file Fig. 1). During Eu adsorption on D231
 103 resin, a triply charged functional group or cation ionized from
 104 the resin, exchanging with Eu in solution. Hydrogen ion con-
 105 centration influenced this ionization: at pH=4, high hydrogen
 106 ion concentration inhibited cation ionization, reducing Eu ad-
 107 sorption and enhancing desorption. Supporting information

108 Fig. 1 shown the adsorption of Eu by D231 resin as a func-
 109 tion of time. Where vertical coordinate was the ratio of Eu
 110 concentration at moment t to its initial concentration[22].
 111 Yu et al.[23] proposed a hypothesis for adsorbent ad-
 112 sorption/desorption. They suggested that, in addition to
 113 binding/separation within internal pores, the liquid membrane
 114 on the adsorbent surface also affected substance diffusion,
 115 this process was named “liquid membrane tidal diffusion
 116 model (LMTD)”. LMTD included two steps as shown in
 117 Fig 1. First step, particles mainly diffused into the liquid
 118 membrane located at the fillings; the particles in liquid
 119 membrane would then be released into the solution. Second
 120 step, particles attached to liquid membrane would further
 121 diffuse into the solid internal hole. Simultaneously, the
 122 particles would then release from the solid internal hole
 123 into the liquid membrane. Afterwards, the liquid membrane
 124 tidal diffusion model was further investigated by Haoqi
 125 Yu et al.[22] and combined with the non-homogeneous
 126 isothermal adsorption to create new kinetic equations,
 127 which successfully described concentration fluctuation in the
 128 adsorption/desorption process.

129 Based on previous researches, this work proposed the fol-
 130 lowing hypotheses: As the mobile phase moved in chro-
 131 matography, a liquid membrane formed on filling surfaces.
 132 Uranyl ions entered and were retained in the liquid mem-
 133 brane. Flowing solution carried away some retained uranyl
 134 ions while continuously delivering new ones into the liquid
 135 membrane. Meanwhile, ²³⁵UO₂²⁺ is lighter than ²³⁸UO₂²⁺,
 136 which cause ²³⁵UO₂²⁺ in the liquid membrane would more
 137 easily be moved into mobile phase. It gradually separated
 138 ²³⁵UO₂²⁺ from ²³⁸UO₂²⁺ in chromatography.

139 2.2 Determination of optimal separation conditions

140 Each pulse is to enter a sample solution, then switch a sec-
 141 tion of air, and then enter the sample solution of the next sec-
 142 tion of pulse. The optimum conditions for uranium isotopes
 143 separation by two chromatographic columns were obtained
 144 through conditional experiments.

145 The flow rate of the mobile phase, pH value and enabling
 146 temperature of dynamics chromatography affect the separa-
 147 tion effect of chromatography to a certain extent. In order to
 148 obtain the optimal separation conditions for the chromatog-
 149 raphy, the researchers prepared 10 test tubes to collect the
 150 chromatographic effluent in equal volumes. The concentra-
 151 tion of ²³⁵U and ²³⁸U in the effluent from each tube (each
 152 tube was a separate section) was determined by Inductively
 153 Coupled Plasma-Mass Spectrometry (ICP-MS, iCAP PROX
 154 Germany), and the separation effect of dynamic chromatog-
 155 raphy was analyzed. For the purpose of better describing the
 156 separation effect of columns on U isotopes, front maximum
 157 enrichment value (β) was used in this paper to judge the chro-
 158 matographic separation ability with different fillings materi-
 159 als under different operating environments [24], Eq (1)

$$160 \beta = \frac{\frac{235}{s}U / \frac{238}{s}U}{\frac{235}{o}U / \frac{238}{o}U} \quad (1)$$

161 where, ²³⁵U/²³⁸U means the isotopic abundance ratio in

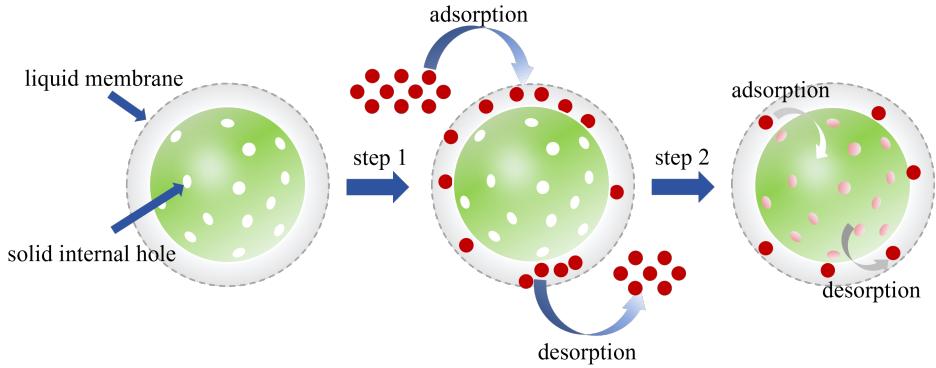


Fig. 1. Schematic diagram of the liquid membrane diffusion tidal model

162 chromatographic effluents and $^{235}U/^{238}U$ means that in orig-
 163 inal $UO_2(NO_3)_2$ solution. β values larger than 1.000 means
 164 that the ^{238}U is preferentially enriched in the liquid phase in
 165 the front band region and ^{235}U is enriched in the membrane.
 166 Average enrichment value ($\bar{\beta}$) was used to judge the chro-
 167 matographic separation efficiency, which is defined as Eq (2)

$$\bar{\beta} = \frac{\sum_{i=1}^n \beta_i}{n} \quad (2)$$

168 where β_i means the enrichment value ($\beta_i > 1$) in the chro-
 169 matographic effluents when the abundance of ^{235}U is higher
 170 than the mean value. Firstly, we performed separation exper-
 171 iments using the columns under a variety of conditions. Sec-
 172 ondly, using the front maximum enrichment value and aver-
 173 age enrichment value enabled a good comparison of the chro-
 174 matographic optimal separation conditions. Thirdly, U iso-
 175 topes were subsequently separated under optimal separation
 176 conditions, the $\beta > 1$ portion of the chromatographic effluent
 177 solution was the gold separation section. After that, the gold
 178 separation section was collected from each chromatographic
 179 separation section was collected from each chromatographic
 180 effluent solution for the next stage of separation, and this op-
 181 eration was cycled to achieve multistage separation. Finally,
 182 based on multiple stages separation experiments, the chro-
 183 matographic separation factor was calculated by using Eq (3).

$$A\alpha^n = B \quad (3)$$

184 where, A means the ratio of the mass of ^{235}U to U in the
 185 initial solution; α is the separation factor; n is the number of
 186 separation stages; B is the ratio of the mass of ^{235}U to U in
 187 the separated solution[25].

III. EXPERIMENTAL

3.1 Reagents and Materials

188 Reagents and materials used in the experiments:
 189 Polyvinyl chloride(PVC) plastic tubes, 1 mm diam-
 190 eter SiO_2 pellets, 1 mm diameter ABS plastic pel-

191 lets, ethanol absolute, hydrochloric acid, uranyl ni-
 192 trate hexahydrate($UO_2(NO_3)_2 \cdot 6H_2O$), uranyl zinc ac-
 193 etate ($ZnUO_2(CH_3COO)_4 \cdot 7H_2O$), cationic surface active
 194 agent(Hexadecyl trimethyl ammonium Bromide $C_{16}H_{33}N(C_2H_5)_3Cl$).
 195 The reagents used were all analytical pure reagents.

3.2 Chromatographic column design

200 Two types of dynamics liquid chromatography were used
 201 in the study, which in this work were referred to as organic
 202 and inorganic columns, respectively. Their parameters are
 203 shown in supplementary file Table 1 and the column struc-
 204 tures are shown in Fig 2.

3.3 Characterization

205 Fourier Transform Infrared (FTIR) spectra for fillings be-
 206 fore and after the separation experiments were obtained on
 207 Thermo Fisher Scientific Nicolet iS20 spectrophotometer
 208 (USA) in the range of 4000-400 cm^{-1} . The Energy Dis-
 209 persive Spectrometer (EDS) and Scanning Electron Micro-
 210 scope (SEM) of chromatographic fillings were carried out on
 211 Hitachi SU8100. X-ray Photoelectron Spectroscopy (XPS,
 212 Thermo Scientific K-Alpha, USA) was used to analyze the
 213 chemical composition of chromatographic fillings before and
 214 after the experiments.

3.4 Design of automatic separation device

215 In order to enable the chromatography to realize auto-
 216 matic control of injection, diversion and collection, we de-
 217 signed a complete automatic separation device, as shown in
 218 Fig 3(a). There are four components of this automatic de-
 219 vice: Adjustable flow systems, Switching pulse injection sys-
 220 tems, Chromatographic separation systems (chromatography
 221 column), Time-controlled automatic shunt. Adjustable flow
 222 system equipped with SC-2556 peristaltic pump is the driv-
 223 ing force of the entire device, which mainly used to trans-
 224 port the sample liquid and control the flow rate of the sample
 225 liquid. Switching pulse injection systems equipped with a
 226 three-way valve to control the gas/liquid switching feed. The
 227 injection time of liquid and gas were determined according
 228 to the experimental results. Chromatographic separation sys-
 229 tem was the central to realize separation of uranium isotopes.
 230 Time-controlled automatic shunt at the end of chromatogra-
 231 phy columns could be operated by timing and timing shunt
 232 through the fluid sensor to realize time-advancing shunt[26].
 233 The switching pulse injection system has two internal pa-

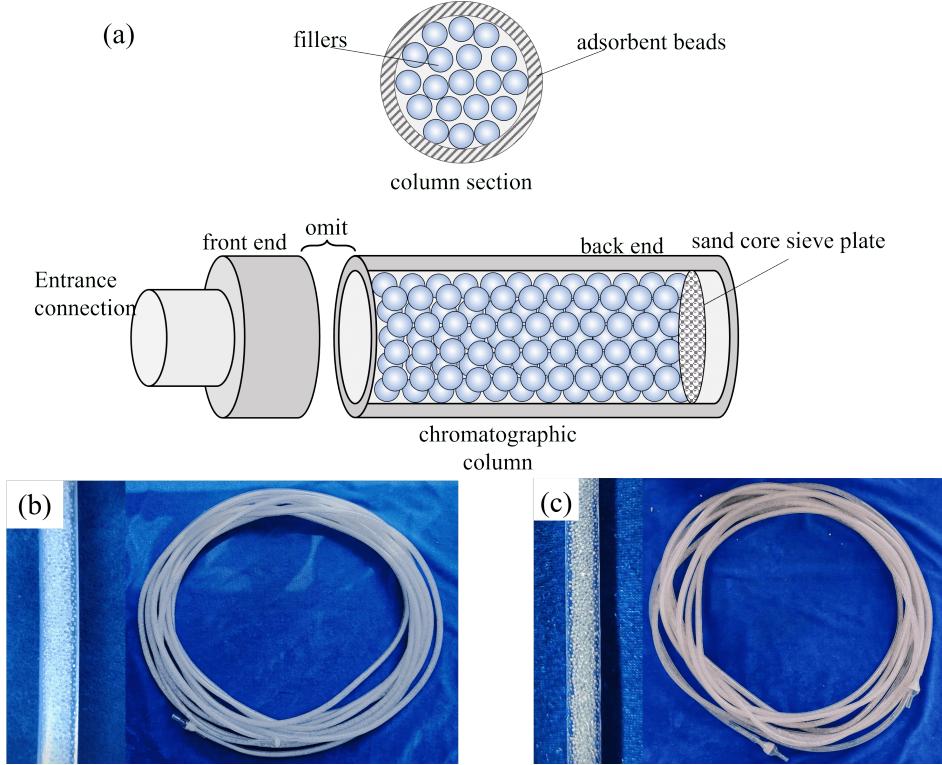


Fig. 2. (a) Schematic diagram of the structure of the column; (b) Physical diagram of the organic column; (c) Physical diagram of the inorganic column

236 parameters, T_1 and T_2 . T_1 means the time of fluid injection
 237 and T_2 means the time of air injection. By using the switch-
 238 ing pulse injection system, the pre-treated sample will be fed
 239 into the column in an alternating air/liquid mode. Accord-
 240 ing to the assumption in 2.3, ^{235}U gradually separates from
 241 ^{238}U as it moves within the column and then first flows out of
 242 the column end. At this point, the time-controlled automatic
 243 shunt automatically diverts a section of aqueous solution with
 244 a higher abundance of ^{235}U , based on the T_3 and T_4 values
 245 obtained from previous conditional experiments. As shown in
 246 Fig 3(b), time-controlled automatic shunt has two parameters:
 247 T_3 and T_4 , which both have initial values. When the air sec-
 248 tion ends and solution flows out from the end of the column,
 249 T_3 begins to count down, and the solution below the average
 250 abundance of ^{235}U flows out of the T_3 outlet. After the T_3
 251 countdown is over, the three-way valve is adjusted to the T_4
 252 position, and the ^{235}U solution with higher abundance flows
 253 out from the T_4 outlet, and the T_4 countdown begins. Until
 254 the T_4 countdown ends, the three-way valve is reset to the T_3
 255 position, and the remaining solution continues to flow out of
 256 the T_3 outlet until the air section of the next pulse. In short,
 257 the separated solution collected by outlet T_4 was the enrich-
 258 ment solution and was collected into the enrichment solution
 259 cells.

260 However, a single stage of separation could not achieve
 261 the ^{235}U abundance for nuclear fuel fabrication, therefore, it
 262 is necessary to install a reflux device outside the chromato-
 263 graphic separation system to achieve multistage separation.

264 Generally, in the n^{th} stage of separation, the adjustable flow
 265 system makes the depleted stream flow back to the $(n-1)^{\text{th}}$
 266 stage sample cell, and the enrichment flows into the cell to be
 267 separated, waiting for the $(n+1)^{\text{th}}$ stage of separation, and so
 268 on[27], as shown in Fig 3(c).

IV. RESULTS AND DISCUSSION

270 4.1 Organic chromatographic column for U isotope sep- 271 aration

272 ABS plastic is a kind of ternary copolymer composed
 273 of any content of acrylonitrile (A), butadiene (B), styrene
 274 ethenylbenzene (S), which has the advantages of strong cor-
 275 rosion resistance, high toughness, and easy-to-obtain raw ma-
 276 terials, etc. This material has a wide range of applications in
 277 the manufacturing industry and chemical industry, including
 278 mechanical, electrical, 3D printing and other manufacturing
 279 industries, as well as in the chemical industry[28–30]. In or-
 280 der to investigate the effect of organic functional groups on
 281 isotope separation, avoid other chemical reactions between
 282 uranyl nitrate and fillings, and enable the fillings to be reused
 283 for a long period of time, the organic columns were packed
 284 with ABS plastic spheres with a diameter of 1.0 mm.

285 In the previous study of this research group[26, 31], re-
 286 searchers have conducted a series of studies on temperature-
 287 enabling kinetic liquid chromatography, since both silica and
 288 ABS fillings are not adsorbent to uranyl ions, so many of

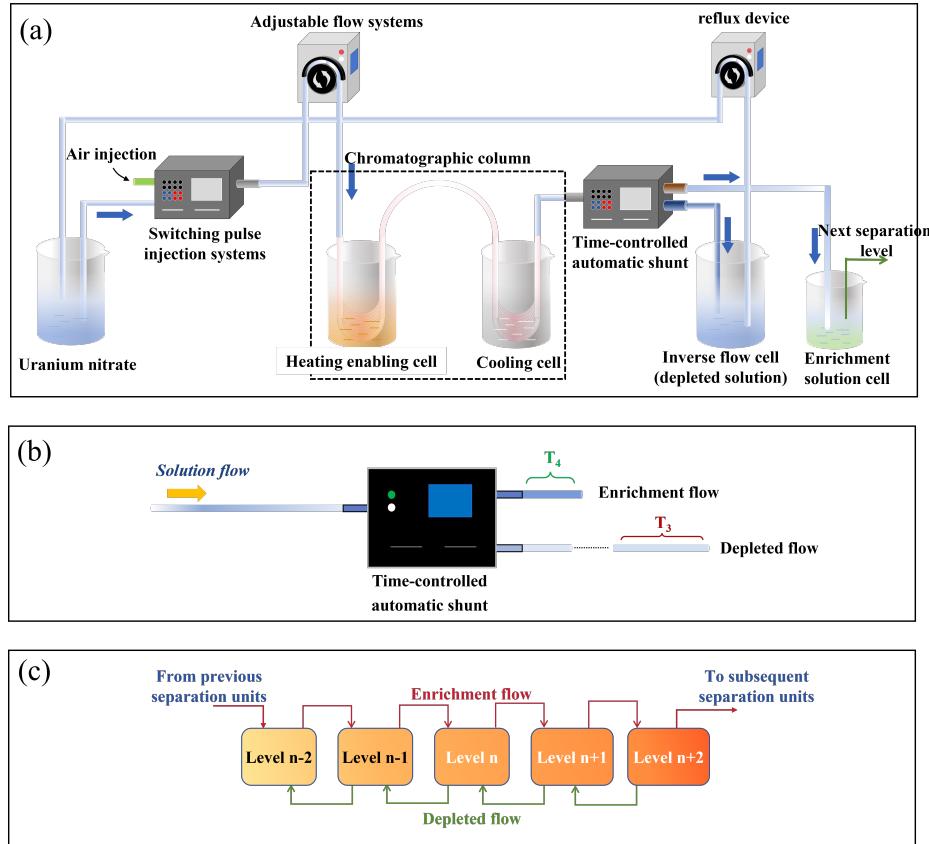


Fig. 3. (a) Schematic diagram of the automatic separation device; (b) separation principle of the time-controlled automatic shunt; (c) Flow chart of chromatographic device multi-stage separates U isotopes

289 working conditions can be followed in this paper. In those
 290 work, the optimal flow rate of the sample inside the 10m-type
 291 column was 5.698 mL/min, but it is obviously not suitable for
 292 organic column with larger internal diameters. The linear ve-
 293 locity of the sample in the column can be calculated by Eq 4
 294 and the sample flow rate suitable for organic columns can be
 295 deduced inversely.

$$296 \quad l = \frac{QH}{V_{column} - V_{fillings}} \quad (4)$$

297 Where, l (cm/min) is the linear velocity of the solution in-
 298 side the column; Q (mL/min) is the flow rate of the solution;
 299 H is the length of the column; V_{column} is the volume of the
 300 column; and $V_{fillings}$ is the total volume of the fillings. The
 301 previous column was calculated that sample flow rate was
 302 15 mL/min. In order to make the flow rate of the mobile
 303 phase of fillings in organic columns same, the flow rate of
 304 mobile phase for the organic column in this paper was also 15
 305 mL/min. The work built on prior experiments, establishing
 306 the injecting mode was set at 20mL (injection) for 80s, and
 307 then switched to gas (air); when the solution flowed out in
 308 strands at the outlet end of the column (gas injection for about
 309 100s), the inlet end of the column was switched to liquid
 310 injection, and this was repeated. These time data were set

311 in the switching injection system (Fig 3(a)) to realize the pur-
 312 pose of gas/liquid switching injection.

313 4.1.1 Characterization of ABS fillings

314 Characterization was carried out on the type chromato-
 315 graphic column fillings before and after separation experi-
 316 ments. SEM-EDS characterization showed that ABS plastic
 317 pellets were in the shape of a sphere with a little layer struc-
 318 ture on the surface, and the surface morphology of the filling
 319 before and after the experiment was almost unchanged, and
 320 the adsorption of elemental U was not observed (at pH=2).
 321 Although the adsorption of U was not detected in the EDS
 322 characterization, XPS results showed that there was still a
 323 trace amount of U(VI) remaining in ABS plastic after the ex-
 324 periment.

325 The description of ABS fillings' characterization is shown
 326 in supplementary file.

327 4.1.2 Effect of pH on separation

328 Comprehensive previous experiences, the pH value of the
 329 solution has a great influence on the separation, ABS plastic
 330 pellets for the first time as a chromatographic filling, to deter-
 331 mine the optimal conditions for its use is crucial. When the
 332 solution pH value is 2.5, the main of uranium in the solution
 333 is uranyl ion (UO_2^{2+}). When $pH > 2.5$, with the increase of pH
 334 value, the uranyl ion (UO_2^{2+}) in the solution begins to hy-
 335 drolyze, forming a multinuclear or even cage structure, and
 336 finally generating the hydroxide precipitation[32]. In order to

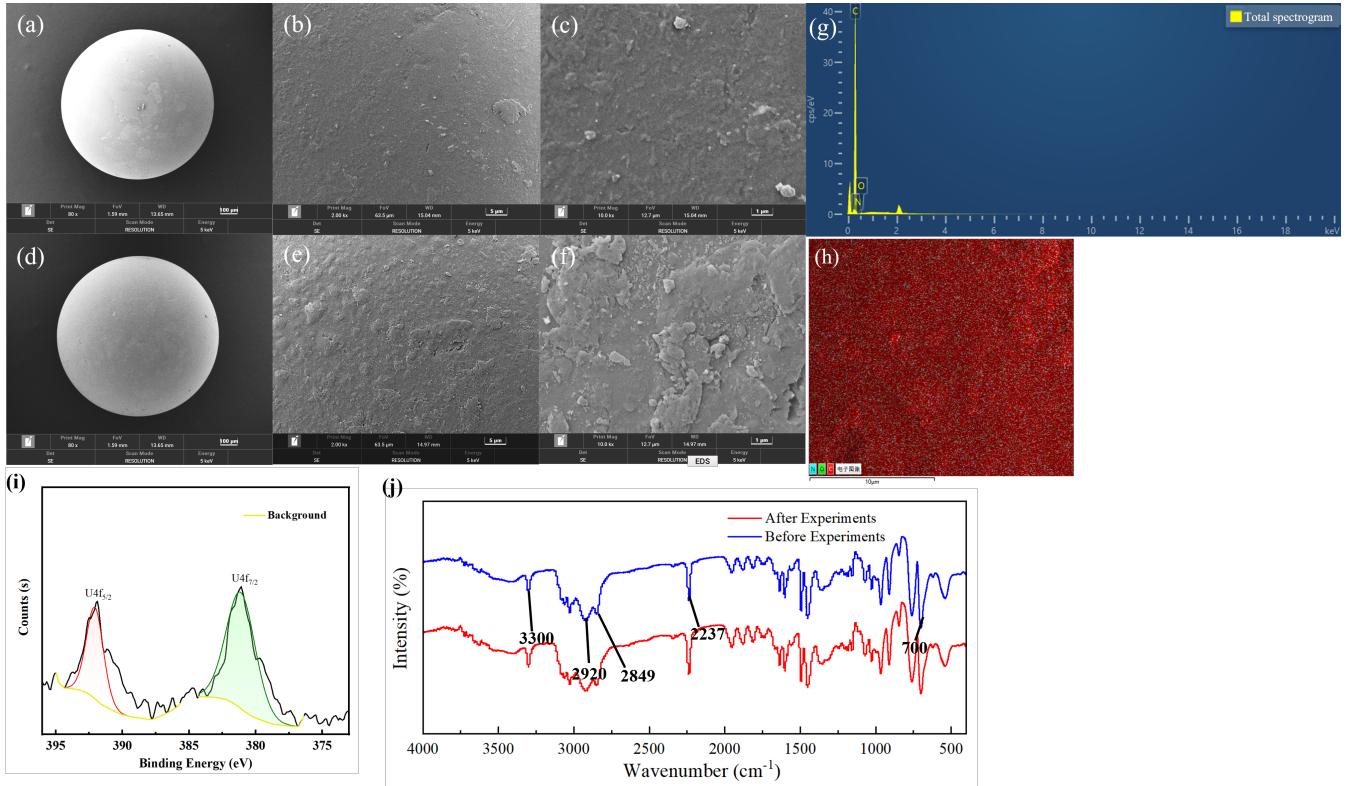


Fig. 4. SEM-EDS characterization of ABS fillings before and after experiments (a) $100\mu\text{m}$ before experiments; (b) $5\mu\text{m}$ before experiments; (c) $1\mu\text{m}$ before experiments; (d) $100\mu\text{m}$ after experiments; (e) $5\mu\text{m}$ after experiments; (f) $1\mu\text{m}$ after experiments; (g) EDS total spectrum after experiments; (h) EDS electronic spectrum after experiments; (i)XPS characterization; (j)FTIR characterization

337 determine the more suitable acidity for organic type columns,
 338 the experiment used uranyl nitrate solution of 15-200ppb and
 339 divided it into three groups with pH values set at 2, 4 and
 340 7, respectively. Meanwhile, in order to exclude other inter-
 341 ferences, the columns were not temperature-enabled in this
 342 experiment, and the results obtained are shown in Fig 5.

343 Measurements of U isotope concentrations using ICP-MS
 344 are subject to some uncertainty. In Fig.9, the light-colored
 345 area indicates the fluctuation ranges of isotope concentration.
 346 Moreover, the quality and dispersion of β_{\max} was analyzed by
 347 type-A uncertainty, which is defined as Eq 5.

$$348 \quad uA = \sqrt{\frac{\sum_{i=1}^n (s_i - \bar{s})^2}{n(n-1)}} \quad (5)$$

349 where, uA stands type-A uncertainty; s_i denotes the i^{th} test
 350 result of a sample; \bar{s} means average value of a sample test; n
 351 is the number of tests for a sample.

352 The results showed that at pH = 2, uranyl ions were mainly
 353 concentrated in the front and back end of the column efflu-
 354 ent, and the best separation section was at the 6 ~ 8 mL and
 355 10 ~ 14 mL, $\beta_{\max} = 1.0243$, $uA=5.4419\times 10^{-2}$, $\bar{\beta} = 1.0150$.
 356 At pH=4, the concentration of uranyl ions fluctuated con-
 357 tinuously with the effluent volume, and the best separation
 358 section was at the 2 ~ 6 mL and 8 ~ 10 mL, $\beta_{\max} =$
 359 1.0175 , $uA=1.7082\times 10^{-2}$, $\bar{\beta} = 1.0093$, and its separation effect

360 was weaker than that of the other two groups of experiments;
 361 At pH=7, uranyl ions were also mainly concentrated in the
 362 first and last of the effluent, and the optimal separation sec-
 363 tion was in the 8 ~ 16 mL, $\beta_{\max} = 1.0242$, $uA=1.2595\times 10^{-2}$,
 364 $\bar{\beta} = 1.0148$. The comprehensive results showed that pH = 2
 365 was the most suitable acidity for the organic type column.

366 At pH=4, the species of uranium in solution are UO_2^{2+} and
 367 $\text{UO}_2(\text{OH})^+$, the internal environment of the chromatographic
 368 column was complicated, resulting in irregular change trend
 369 of U isotope concentration, as shown in Fig 5(b), and the de-
 370 gree of enrichment is lower than the other two groups, pH=2
 371 and pH=7. Because of the existence of liquid membrane and
 372 the adsorption of uranium by ABS fillings, the uranium in
 373 the solution remained in the residual liquid membrane on the
 374 surface of the fillings every time the solution flows through
 375 the chromatographic column. At the same time, the chro-
 376 matographic injection method used in this paper is gas/liq-
 377 uid switching injection (1.2), which makes the next solution
 378 pulse through the column will carry the residue of the previ-
 379 ous solution pulse. At pH=7, the main species of U were UO_2
 380 $(\text{OH})_2$, therefore, compared with pH=4, the concentration of
 381 U changes more regularly. From Fig 5(a) (c), it can be clearly
 382 observed that the concentration of U with the change of efflu-
 383 ent volume showed a trend of decreasing and then increasing,
 384 the concentration of the first section of the chromatographic
 385 effluent volume is generally higher, indicating that there will
 386 be a residue in the solution flow through the column, and af-

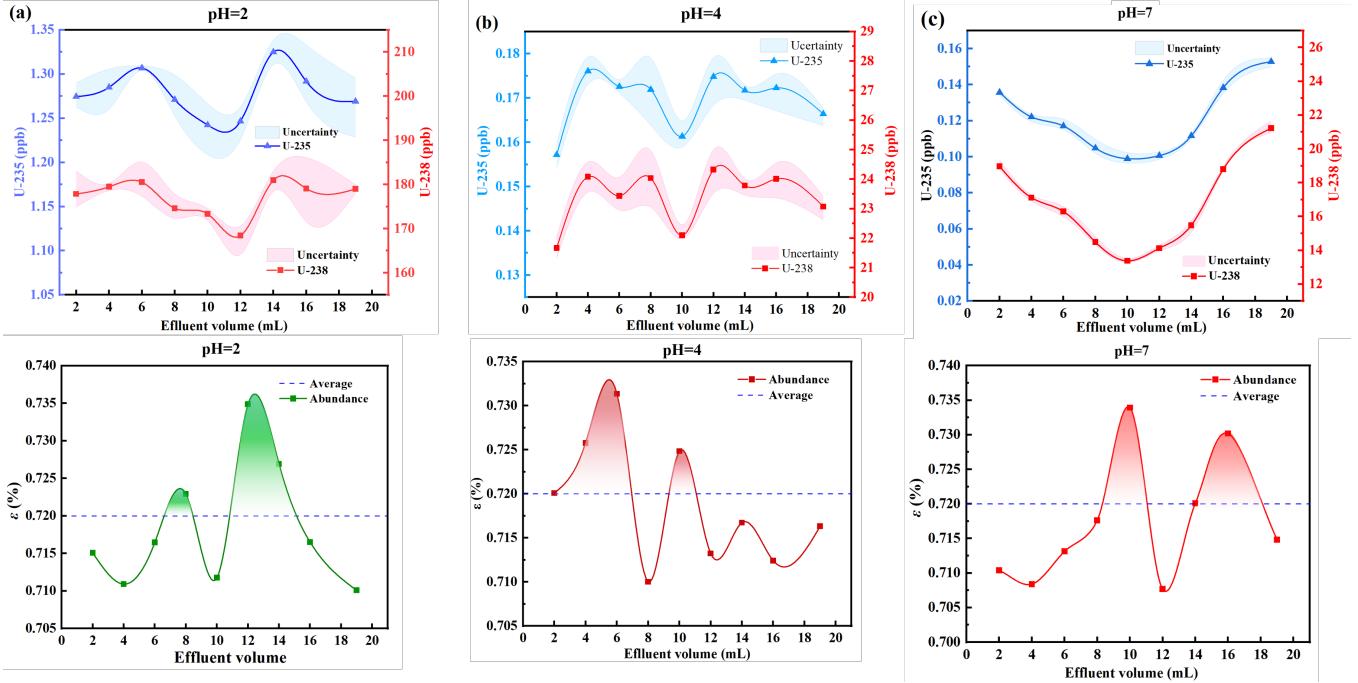


Fig. 5. Effect of pH on the concentration of U isotopes and abundance of ^{235}U in chromatographic column. (a) pH=2; (b) pH=4; (c) pH=7

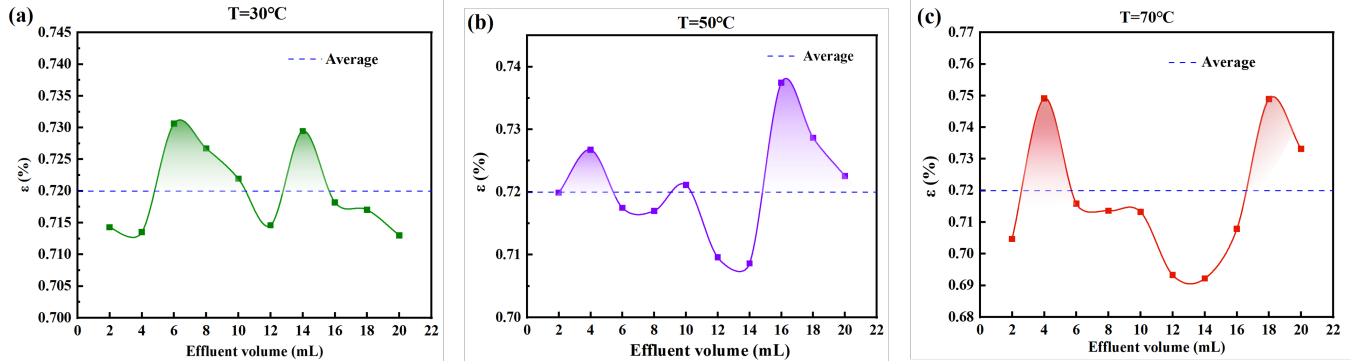


Fig. 6. Effect of temperature on the separation of uranium isotopes (a) $T=30^\circ\text{C}$; (b) $T=50^\circ\text{C}$; (c) $T=70^\circ\text{C}$

387 ter chromatographic separation, the concentration of U will
388 be concentrated in the second half.

389 4.1.3 Effect of enabling temperature on separation

390 In this paper, the pipe used for preparing the chromatographic
391 column is made of PVC material, which has high
392 toughness, transparency and corrosion resistance, and the
393 pipe wall thickness is only 2 mm, so the column can be
394 temperature-enabled well. In the experiment, the solution
395 temperature has a great influence on the functional groups
396 on the fillings surface and the formation of the liquid mem-
397 brane. By heating and cooling organic-type column using the
398 temperature-enabling cell in Fig 3(a), the flow of uranyl ions
399 blocked by column fillings will change periodically, which
400 will facilitate the separation of U isotopes. Theoretically, the
401 larger the temperature difference between the enabling and
402 cooling cell, the more significant the gain in U isotope sep-
403 ration, but when the temperature reaches 75°C or more ABS

404 plastic will deform[33, 34]. Therefore, in this paper, 30°C,
405 50°C, and 70°C were used to be the enabling temperature of
406 the chromatography. In the experiment, uranyl nitrate solu-
407 tion of 50 ppb and pH=2 was used as the sample to be sep-
408 rated, and the separation results were shown in Fig 6.

409 The results showed that the best separation sections of U
410 isotopes on the organic column after temperature enabling
411 were concentrated at the front and rear ends of the effluent
412 volume, which were calculated as follows: $\beta_{\max} = 1.0150$ and
413 $\bar{\beta} = 1.0101$ at $T = 30^\circ\text{C}$; $\beta_{\max} = 1.0231$ and $\bar{\beta} = 1.0117$
414 at $T = 50^\circ\text{C}$; and $\beta_{\max} = 1.0449$ and $\bar{\beta} = 1.0373$ at
415 $T = 70^\circ\text{C}$. With the increase of assignment temperature, the
416 separation efficiency of organic column for U isotopes was
417 also increased. The maximum enrichment and average en-
418 richment were much larger than those of other groups when
419 the enabling temperature was 70°C. Therefore, 70°C was se-
420 lected as the best separation enabling temperature, and 2 ~ 4

Table 1. Experimental data and results of the organic chromatographic column

test	Solution flow rate	Solutions and pH	Enabling temperature	Maximum front enrichment value /separation factor	Type-A uncertainty	Average enrichment
Enabling Temperature Conditions Experiment		Uranyl nitrate solution pH=2 pH=4 pH=7	without temperature-enabling	$\beta_{max} = 1.0250$ $\beta_{max} = 1.0180$ $\beta_{max} = 1.0242$	5.4419×10^{-2} $\bar{\beta} = 1.0156$ 1.7082×10^{-2} $\bar{\beta} = 1.0126$ 1.2595×10^{-2} $\bar{\beta} = 1.0148$	
pH value conditioned experiment	15mL/min	Uranyl nitrate solution pH=2	30°C 50°C 70°C	$\beta_{max} = 1.0150$ $\beta_{max} = 1.0236$ $\beta_{max} = 1.0445$	- $\bar{\beta} = 1.0101$ $\bar{\beta} = 1.0116$ $\bar{\beta} = 1.0373$	
multistage separation test		Uranyl nitrate solution pH=2	70°C	$\bar{\alpha} = 1.0184$	5.4816×10^{-5}	-

421 mL and 16 ~ 20 mL were the best separation sections for the
422 chromatographic effluents.

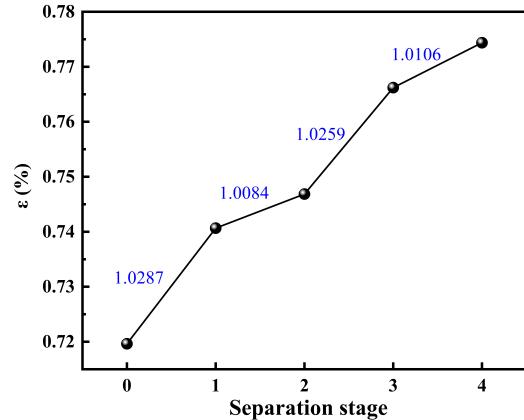
423 In section 2.1, the theory indicated that $^{235}\text{UO}_2^{2+}$ is lighter
424 than $^{238}\text{UO}_2^{2+}$, which cause $^{235}\text{UO}_2^{2+}$ in the liquid membrane
425 would more easily be moved into mobile phase and the ^{235}U
426 abundance in first few chromatography effluent should be
427 higher. However, in the first few chromatography effluents
428 (Fig. 5, 6) were lower than 0.72%. Actually, this
429 phenomenon is correct. Since the sample was pulsed in the
430 experiment, the previous pulse will remain on the column
431 filling surface, and the residual solution will have a lower
432 abundance of ^{235}U and a higher abundance of ^{238}U . This was
433 reflected in the abundance of ^{235}U below 0.72% in the first
434 few experimental data points.

4.1.4 Multi-stages separation experiments

435 Through the above condition experiments, this paper finally
436 determined the optimal working conditions of the organic
437 column as: solution flow rate of 15 mL/min, $pH = 2$,
438 enabling temperature of 70°C, and the optimal separation
439 segments in the chromatographic effluent volume of 2 ~ 4
440 mL and 16 ~ 20 mL. The effluent can be accurately collected
441 using the time-controlled automatic shunt system in Fig 3(a).
442 The original sample was uranyl nitrate solution with a natural
443 abundance of 50 ppb, and the experimental results are
444 shown in Fig 7, $\alpha_1 = 1.0287$, $\alpha_2 = 1.0084$, $\alpha_3 = 1.0259$,
445 $\alpha_4 = 1.0106$, $\bar{\alpha} = 1.0184$, and type-A uncertainty was
446 5.4816×10^{-5} . In this way, the abundance of ^{235}U could reach
447 3% through 79 stages separation. The results showed that the
448 abundance of ^{235}U continued to increase during the step-by-step
449 separation, but the separation factors of stage 2 and stage
450 4 are relatively small. Moreover, compared with that in 3.1.3,
451 the separation factors were inferior to that in one stage separation.
452 The reason for this phenomenon may be due to the presence
453 of a three-way valve in the time-controlled shunt system
454 at the outlet end of the column, in which the outflow solution
455 produces a Bernoulli phenomenon, which leads to a reduction
456 in the flow rate of the solution, stagnation, and mixing of the
457 front and back solutions, which results in a decrease in the
458 abundance. Table 1 shows all the experiments done with the
459 organic column. And type-A uncertainty is also displayed in
460 it.

4.2 Inorganic chromatographic column for U isotope separation

461 In the previous work of researchers[26, 31], the column
462 was filled with SiO_2 pellets. Therefore, some experimental

Fig. 7. ^{235}U abundance under multi-stages separation

466 conditions were followed in this paper for the study of inorganic
467 chromatographic columns, and the working conditions
468 were set as follows: solution flow rate of 15 mL/min, $pH=2$,
469 and temperature of the enabling cell at 50°C.

4.2.1 Characterization of SiO_2 before and after experiments

470 SEM-EDS characterization showed that the inorganic
471 fillings(SiO_2) were smooth spheres, the surface of the fillings
472 was still smooth after separation experiments, and no U adsorption
473 was observed. The FTIR results indicated that hydroxyl groups
474 were produced on the surface of the SiO_2 filling after the experiment.
475 And XPS determination showed the filling has a trace adsorption of uranium after experiments.

476 The characterization results of SiO_2 fillings were shown in
477 supplementary figure 2.

4.2.2 Single separation of uranium isotopes

478 Uranyl nitrate solution of 50ppb and $pH=2$ was used as the
479 separation sample solution. The column enabling temperature
480 was 50°C and the injection rate was 15 mL/min. The effluent
481 was collected at the exit of the chromatographic column
482 every 2 mL, and a total of 11 samples (including the original
483 solution) were detected by an inductively coupled plasma
484 mass spectrometer (model: ICAPRQ02625), and the results
485 were shown in Fig 8. It can be seen from the results that the

490 separation effect of ^{235}U and ^{238}U is significant in the 5 ~ 11
 491 mL of the chromatographic effluent, so the optimal separa-
 492 tion of U isotopes in the inorganic column is the 5 ~ 11 mL.
 493 In Fig 8(b), The enrichment reached the maximum at the ef-
 494 fluent of 10 mL, i.e., $\beta_{\max} = 1.0171$. While in the optimal
 495 separation section, $\bar{\beta} = 1.0142$.

496 In addition, regarding Fig 8(b), adsorption of uranyl ions
 497 by silanol groups on the surface of SiO_2 filling causes ^{235}U
 498 to have a longer retention time in the column. As a result,
 499 uranium abundance appeared in the middle-to-late section of
 500 the chromatographic effluent volume, and the double-peaks
 501 overlap.

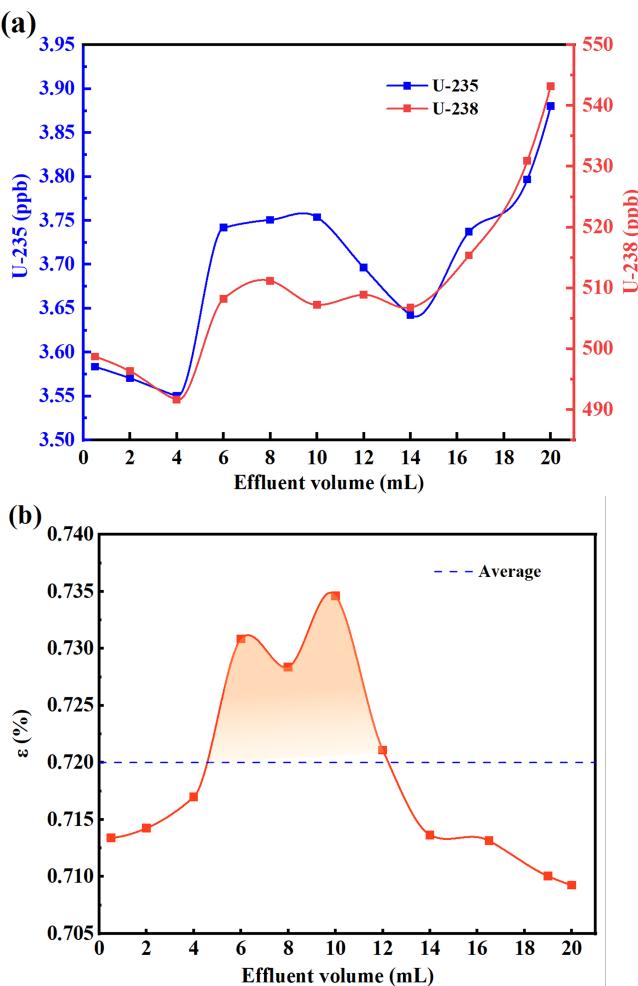


Fig. 8. (a) Concentration of ^{235}U and ^{238}U in effluent solution with effluent volume; (b) Abundance of ^{235}U in effluent solution with effluent volume

4.2.3 Multi-stages separation experiments

502 According to the work in section 4.2.2, the best separation
 503 section for U isotopes is in the 5 ~ 11 mL of the chromato-
 504 graphic effluent, which means that after each stage of separa-
 505 tion, the middle 3/10 of the solution can be collected as the
 506 enrichment solution. The self-constructed automatic control
 507 shunt system could well realize the automatic separation of
 508 each section of the effluent, and realize automated and con-

510 tinuous work, and no manual duty required.

511 After four stages of separation, the results were shown in
 512 Fig 9. Calculating the separation factors for each stage by
 513 Eq 3, it had been obtained that $\alpha_1 = 1.007$, $\alpha_2 = 1.004$, α_3
 514 = 1.02, $\alpha_4 = 1.009$, and $\bar{\alpha} = 1.011$, which was not as good
 515 as the organic column, but comparable to the gas diffusion
 516 method. To achieve ^{235}U abundance of 3%, a 112-stage sep-
 517 aration should be required. The results showed that the abun-
 518 dance of ^{235}U continued to increase during the stepwise sep-
 519 aration. Similar to the organic columns, the second stage of
 520 separation remained the least effective.

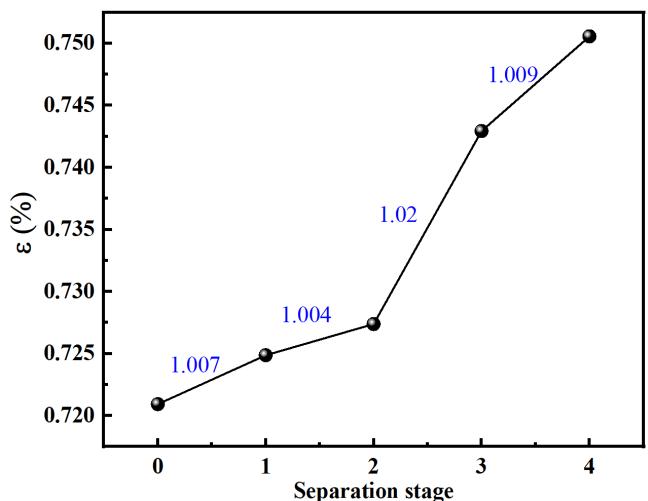


Fig. 9. Multi-stage separation of uranium isotopes by inorganic column

4.2.4 Experiments in strong acid environments

521 According to the characterization in 3.2.1, a small amount
 522 of silica hydroxyl groups generated on the surface of SiO_2
 523 filling during the separation process (Fig 8). In order to ver-
 524 ify the importance of silica hydroxyl groups in the separation
 525 process, in this paper, the pH value of the solution to be sepa-
 526 rated was adjusted to 0.1, in which case the silica hydroxyl
 527 groups on the surface of SiO_2 were suppressed to a great
 528 extent[35], which was used to determine the effect of silica
 529 hydroxyl groups on the separation(Fig 10). Experimentally,
 530 15ppb, pH=0.1 uranyl nitrate solution was used as the sep-
 531 aration sample solution, and other working conditions were
 532 consistent with 3.2.2, and the experimental results are shown
 533 in Fig 11.

534 As can be seen in Fig 11(a), the concentration trends of
 535 ^{235}U and ^{238}U were nearly the same, $\beta_{\max} = 1.0122$ and $\bar{\beta}$
 536 = 1.0056. The difference from that in Experiment 3.1 was
 537 very large, the separation efficiency was poor, and the abun-
 538 dance change curves (Fig 11(b)) did not form a regular peak.
 539 Therefore, when the silica hydroxyl group was inhibited dur-
 540 ing the separation process, the separation effect was insignifi-
 541 cant, which successfully proved that the presence of silica hy-
 542 droxyl group had a positive benefit on the separation effect.
 543 In other words, moderate acidity (pH=2 or so) is favorable
 544 for the separation of U isotopes; too high acidity (pH<0.1) is
 545 unfavorable for the separation of isotopes.

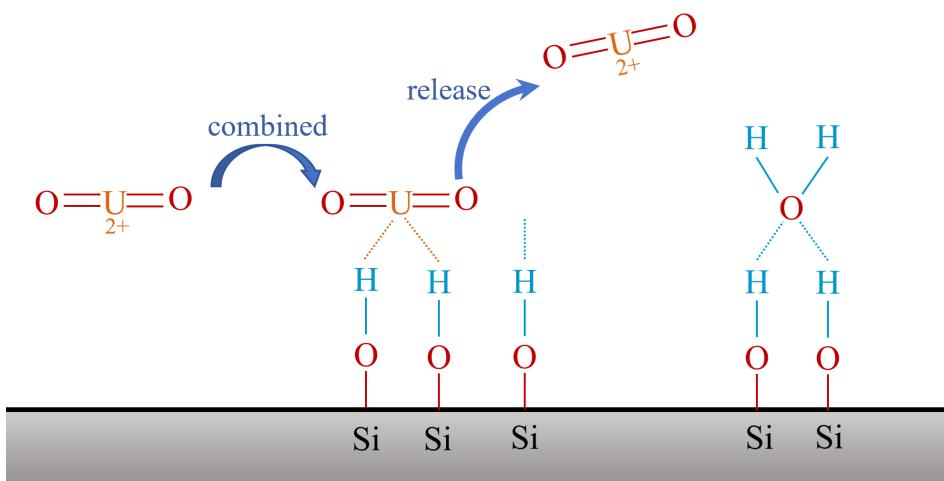


Fig. 10. Behavior of uranyl ions passing through silicon hydroxyl

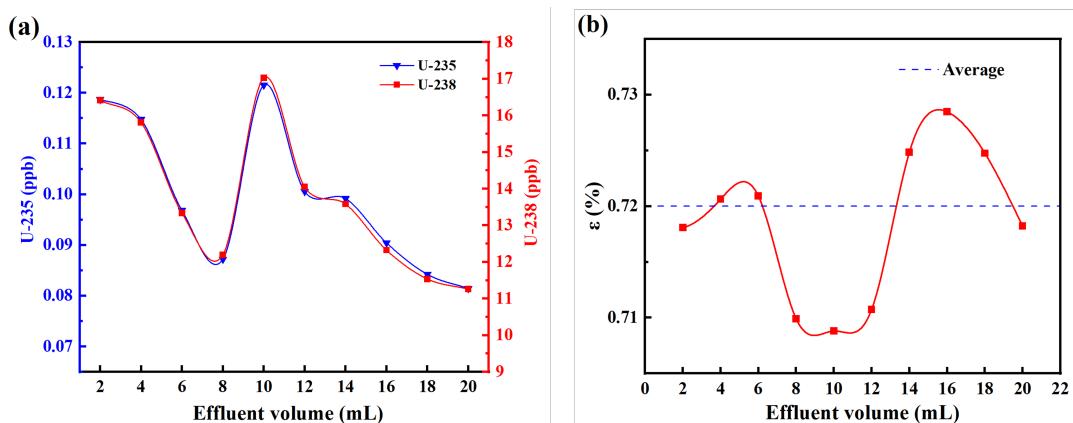


Fig. 11. Effect of silicon hydroxyl group on separation at pH 0.1. (a) Variation of uranium isotopes at the effluent end of the chromatographic column; (b) Distribution of 235U in the chromatographic column

4.3 Separation mechanisms

The experiments in 3.1 and 3.2 had demonstrated that organic and inorganic chromatographic column were able to separate U isotopes efficiently, but the separation mechanisms still need to be explored. In the following, a series of experiments are designed to verify the hypotheses made in the previous section: 1. A liquid membrane will be generated between the fillings and the mobile phase within the chromatography, which will have different blocking effects on particles with different masses; 2. There is a process of trapping and releasing of flow-through particles by the functional groups generated on the surface of the fillings.

In order to verify that the column can separate other particles with different mass, the U-Zn separation experiment was designed in this work. A 50ppb solution of zinc uranyl acetate, pH=2, was used as the sample to be separated, and the experimental conditions were the same as those in 3.1. Because the relative atomic mass of UO_2^{2+} in the solution is 270 and that of Zn^{2+} is 65.38, both of them have the same valence, neither of them reacts chemically with other substances

within the chromatogram, and the difference in mass is obvious, which is well in line with the requirements of the validation experiment. The distribution of Zn and U in the effluent was shown in Fig 12(a)(b).

Eq 1 was modified to the following form for use in describing the capacity of chromatography on the separation of U and Zn:

$$\beta = \frac{s\text{Zn}/s\text{U}}{\text{oZn}/\text{oU}} \quad (6)$$

In Eq 6, $s\text{Zn}/s\text{U}$ is the mass concentration ratio of Zn-U in the chromatographic effluent. oZn/oU is the mass concentration ratio of Zn-U in the original sample. It was calculated that $\beta_{max} = 1.3253$. Compared with the U isotopes, the mass difference between UO_2^{2+} and Zn^{2+} is much larger and the separation effect is more obvious. It was also proved that the liquid membrane can effectively separate ions of different masses.

Otherwise, to verify the role of the liquid membrane in sep-

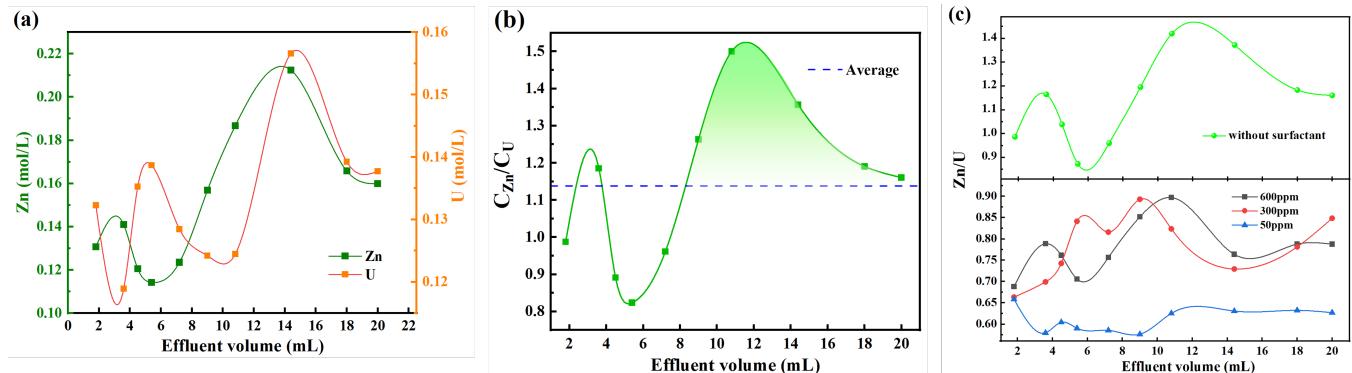


Fig. 12. (a) Concentration changes of U and Zn in column effluent; (b) Distribution of Zn-U in chromatographic column

Table 2. Data and parameters of inorganic chromatographic column separation experiments

test	flow rates	Solutions and pH	enabling temperature	Maximum front enrichment value /Separation factor	Average enrichment
U isotopes primary separation		Uranyl nitrate solution pH=2		$\beta_{max} = 1.0224$	$\bar{\beta} = 1.0162$
U isotopes multistage separation	15mL/min	Uranyl nitrate solution pH=2		$\bar{\alpha} = 1.011$	-
Strong acid environment		Uranyl nitrate solution pH=0.1	50°C	$\beta_{max} = 1.0122$	$\bar{\beta} = 1.0068$
Zn-U separation		Zinc uranyl acetate solution pH=2		$\beta_{max} = 1.3253$	-
surfactant		Zinc uranyl acetate solution (add surfactant) pH=2	50ppm 300ppm 600ppm	$\beta_{max} = 1.0773$ $\beta_{max} = 1.1394$ $\beta_{max} = 1.1519$	-

584 aration process, the experiment used 50ppb, pH=2 solution of 584 zinc uranyl acetate as the sample, adding different concentra- 585 tions of cationic surfactant (cetyltrimethylammonium chlo- 586 ride: $C_{19}H_{42}ClN$) in the sample, to observe the influence of 587 the change of the liquid membrane on the separation effect, 588 and the results of the experiments were shown in Fig 12(c).

589 The structure of surfactants can be viewed as a match-like 589 configuration, shown in supplementary file Fig. 3(a). The 590 "matchstick" as a hydrophobic group repels water molecules, 591 such as R-(alkyl), while the hydrophilic group is the "match- 592 head" which attracts water molecules, such as -OH, -NH₂. 593 This special structure makes the surfactant molecule soluble 594 in water at one end and tends to escape from water at the other 595 end, so as to reduce the tension between water molecules. 596 When used in the mobile phase of a chromatographic col- 597 umn, the liquid membrane formed on the fillings surface is 598 affected[36], as shown in supplementary file Fig. 3(b).

599 The experimental results showed that the separation ef- 600 fect of chromatography was very poor when the concentra- 601 tion was 50 ppm, and β_{max} was only 1.0773; when the 602 concentration was 300 ppm, the separation effect of chromatog- 603 raphy was better, and β_{max} could reach 1.1394; when the 604 concentration was 600 ppm, the separation effect was de- 605 creased $\beta_{max} = 1.1519$. At the same time, with the increase 606 of the concentration of the surfactant, the formation of mi- 607 celles within the mobile phase, which substantially increased 608 the flow impedance, and Zn was significantly more affected 609 than UO^{2+} , and the position of the chromatographic peak 610 was shifted backwards. The reason was as followed: When 611

612 the concentration of surfactant was 50ppm, the water tension 613 was unevenly weakened, the liquid film became irregular and 614 thin, the separation effect was greatly reduced, so there was 615 no obvious chromatographic peak in the effluent curve. At 616 300ppm, the surfactant groups were all over the surface of 617 the packing material, and the ions in the mobile phase were 618 subjected to increased resistance. Although there was a sep- 619 aration effect, the outflow curve of the experimental results 620 could not form regular chromatographic peaks. When the 621 concentration of surfactant was 600ppm, the surfactant in the 622 solution would exist in the form of micelles, and the resis- 623 tance to flow would further increase, and there would be ob- 624 vious double chromatographic peaks. Finally, the experiment 625 was successful to prove the participation of liquid membrane 626 in the separation process. It was experimentally verified that 627 the inorganic column was effective for the separation of U 628 isotopes, and the abundance of U isotopes showed an increas- 629 ing trend in the multi-stage separation experiments, which is 630 expected to realize the industrialized production. The hypoth- 631 esis of the liquid membrane model proposed in the previous 632 paper was also verified, and the chromatographic separation 633 mechanism was explored. Table 2 shows the relevant experi- 634 mental parameters of this paper using inorganic column.

636

V. CONCLUSION

637 In this paper, chromatographic columns with two types
 638 of organic and inorganic fillings were prepared and applied
 639 to the U isotopes separation work to obtain the separation
 640 efficiency and the separation mechanism was discussed.
 641 ABS plastic as fillings for organic column are cost-effective
 642 and flexible, ideal for prolonged use, which could reach a
 643 separation factor greater than inorganic column. However,
 644 it has exhibit lower mechanical strength, and limited surface
 645 modification options. SiO_2 pellets as fillings for inorganic
 646 column offer high mechanical strength, excellent chemical
 647 stability, and large surface area. Nevertheless, they are
 648 potentially brittle and the inorganic column's separation
 649 efficiency was not as good as the organic column.

650 In organic column experiments, the chromatography
 651 optimal working condition were as follow: injection flow
 652 rate=15 mL/min, pH=2, enabling temperature=70°C and
 653 the golden separation segments were 35 mL and 1720 mL
 654 from the chromatographic effluent. Multi-stage separation
 655 experiments showed U isotopes separation factor was 1.0184,
 656 and 79 separation stages were needed for ^{235}U abundance
 657 reach to 3%.

658 According to inorganic column experiments, the chro-
 659 matography optimal working conditions were firstly deter-

660 mined by previous studies, which were as follow: injection
 661 flow rate=15 mL/min, pH=2, enabling temperature=70°C and
 662 the golden separation segments were 511mL from the chro-
 663 matographic effluent. Multi-stage separation experiments in-
 664 dicated that U isotopes separation factor was 1.011, and 113
 665 separation stages were required for enriching ^{235}U abundance
 666 to 3%.

667 Based on characterization results and separation
 668 mechanism experiments, liquid membranes and surface
 669 functional groups on fillings did participate in separation
 670 processes. For industrial production, uranyl nitrate
 671 feedstock could be applied directly, potentially skipping
 672 UF_6 preparation in gas centrifugation. SEM-EDS, XPS, and
 673 FTIR analyses showed SiO_2 and ABS adsorb slight amounts
 674 of uranium without affecting fillings properties, allowing
 675 long-term column reuse. Therefore, combining organic
 676 and inorganic dynamic liquid chromatography provides
 677 a cost-effective, eco-friendly, and efficient method for U
 678 isotope separation. The researches also provided new ideas
 679 for the chromatography and isotope separation field.

VI. REFERENCES

681 [1] Krass A. S., Boskma P., Elzen B., et al., Uranium en- 713 cess. Proceedings of the international symposium on isotope
 682 richment and nuclear weapon proliferation. Routledge, 2020. 714 separation and chemical exchange uranium enrichment, 1992.
 683 <https://doi.org/10.2307/2618941> 715 [11] White D. A., Fathurachman, Design of a Mixer Settler
 684 [2] Jensen R. J., Sullivan J. A., Finch F. T., Laser isotope sepa- 716 Plant for Isotope Separation by Chemical Exchange. Nuclear
 685 ration. Separation Science and Technology, **15**(3): 509–532, 717 Technology, **110**(2): 220–227, 1995.
 686 1980. https://doi.org/10.1007/bf007411-2_281 718 <https://doi.org/10.13182/NT95-A35119>

687 [3] Zeng Tie, An overview of uranium and uranium en- 719 [12] Makarov G. N., Low energy methods of molecular laser
 688 richment and its methods. Journal of Hunan Insti- 720 isotope separation. Physics-Uspekhi, **58**(7): 670, 2015.
 689 tute of Industrial Technology, **13**(01): 6–10+34, 2013. 721 <https://doi.org/10.3367/UFNe.0185.201507b.0717>

690 [4] Glaser A., Characteristics of the gas centrifuge for uranium 722 [13] Whitaker J. M., McGirl N. A., Tucker D., et al., Uranium
 691 enrichment and their relevance for nuclear weapon prolif- 723 enrichment plant characteristics - A training Manual for the
 692 eration. Science & Global Security, **16**(1–2): 1–25, 2008. 724 IAEA. Oak Ridge National Lab.(ORNL), Oak Ridge, TN
 693 <https://doi.org/10.1080/08929880802335998> 725 (United States), 2019. <https://doi.org/10.2172/1606938>

694 [5] Marrero T. R., Mason E. A., Gaseous diffusion coefficients. 726 [14] Wang Yan, Kang Jing, Yang Jie, et al., Study on reuse
 695 Journal of Physical and Chemical Reference Data, **1**(1): 3–118, 727 routes of depleted uranium hexafluoride and its conversion
 696 1972. <https://doi.org/10.1063/1.3253094> 728 products. China Radiation Health, **28**(06): 691–694, 2019.
 697 [6] Snyder R., A proliferation assessment of third gen- 729 <https://doi.org/10.13491/j.issn.1004-714x.2019.06.025>

698 [7] Makarov G. N., Towards molecular laser separation of uranium 730 [15] Boyes B. E., Walker D. G., McGeer P. L., Separation of large
 702 isotopes. Uspekhi Fizicheskikh Nauk, **192**(6): 569–608, 2022. 731 DNA restriction fragments on a size-exclusion column by a
 703 <https://doi.org/10.3367/ufne.2021.02.038942> 732 nonideal mechanism. Analytical Biochemistry, **170**(1): 127–
 704 [8] Raica P., Axente D., Analysis of ^{235}U Enrichment by 733 134, 1988. [https://doi.org/10.1016/0003-2697\(88\)90099-1](https://doi.org/10.1016/0003-2697(88)90099-1)

705 [9] Fujine S., Naruse Y., Shiba K., Analysis of Uranium Isotope 734 [16] Peyrin E., Guillaume Y. C., Villet A., et al., Mechanism
 706 Separation by Redox Chromatography. Nuclear Technology, 735 of DNA hydrodynamic separation in chromatography. Analytical
 707 **62**(3): 317–324, 1983. <https://doi.org/10.13182/NT83-A33255> 736 Chemistry, **72**(4): 853–857, 2000.
 708 [10] Dujardin T., Lonchampt G., Review of the French Chemex pro- 737 <https://doi.org/10.1021/ac990841s>

709 [17] Striegel A. M., Brewer A. K., Hydrodynamic chromatography. 738 [18] Striegel A. M., Hydrodynamic chromatography: packed
 710 Annual Review of Analytical Chemistry, **5**(1): 15–34, 2012. 739 columns, multiple detectors, and microcapillaries. Analytical
 711 <https://doi.org/10.1021/ac00245a001> 740 and Bioanalytical Chemistry, **402**: 77–81, 2012.
 712 [18] Striegel A. M., Hydrodynamic chromatography: packed 741 <https://doi.org/10.1007/s00216-011-5334-3>

745 [19] Gritti F., Wyndham K., Retention mechanism in com- 785 [28] Olivera S., Muralidhara H. B., Venkatesh K., et al., Plat-
746 bined hydrodynamic and slalom chromatography for ana- 786 ting on acrylonitrile–butadiene–styrene (ABS) plastic: a re-
747 lyzing large nucleic acid biopolymers relevant to cell and 787 view. *Journal of Materials Science*, **51**: 3657–3674, 2016.
748 gene therapies. *Journal of Chromatography A*, 2024: 465075. 788 <https://doi.org/10.1007/s10853-015-9668-7>

750 [20] Gritti F., Theoretical predictions to facilitate the method devel- 789 [29] Nan Ting-Ting, Qi You-Guo, Li Xin, et al., Preparation
751 opment in slalom chromatography for the separation of large 790 of weathering-resistant ABS resin and its properties. *Mod-
752 DNA molecules. *Journal of Chromatography A*, **1736**: 465379, 791 ern Plastics Processing Applications*, **34**(05): 20–23, 2022.
753 2024. <https://doi.org/10.1016/j.chroma.2024.465379> 792 <https://doi.org/10.19690/j.issn1004-3055.20210217>

754 [21] Horvath C., Melander W., Liquid chromatography 793 [30] Verma P., Ubaid J., Schiffer A., et al., Essential work of frac-
755 with hydrocarbonaceous bonded phases: theory and 794 ture assessment of acrylonitrile butadiene styrene (ABS) pro-
756 practice of reversed phase chromatography. *Journal 795 cessed via fused filament fabrication additive manufacturing.*
757 of Chromatographic Science, **15**(9): 393–404, 1977. 796 *The International Journal of Advanced Manufacturing Tech-
758 <https://doi.org/10.1093/chromsci/15.9.393> 797 nology*, **113**: 771–784, 2021. <https://doi.org/10.1007/s00170-020-06580-4>

759 [22] Yu H. Q., Yu T., Ye J. H., A new liquid membrane diffu- 799 [31] Fu Yu-Jie, Yu T., Ye J. H., Rapid uranium extraction from
760 sion model for characterizing the adsorption kinetics of eu- 800 seawater by fugitive kinetic chromatography. *Nuclear Technol-
761 ropium by using a continuous measurement of adsorption 801 ogy*, **47**(02): 123–138, 2024. <https://doi.org/10.11889/j.0253-3219.2024.hjs.47.020603>

762 platform. *Nuclear Science and Techniques*, **35**(1): 7, 2024. 802

763 <https://doi.org/10.1007/s41365-024-01361-0>

764 [23] Yu T., Xu Z., Ye J. H., Adsorption kinetics of Eu(III) and 803 [32] Xiaomeng W., Hongxue L., Rui W., et al., The Effect of
765 Am(III) onto bentonite: analysis and application of the liq- 804 Initial Concentration and pH Value of the Uranyl Nitrate
766 uid membrane tidal diffusion model. *Journal of Radioan- 805 Solution on the Its Hydrolysis Reaction*. *Journal of Liaon-
767 alytical and Nuclear Chemistry*, **319**(3): 749–757, 2019. 806 ing University of Petroleum & Chemical Technology, **35**(5):
768 <https://doi.org/10.1007/s10967-018-6386-z> 807 18, 2015. <http://journal.lnpu.edu.cn/EN/10.3969/j.issn.1672-6952.2015.05.005>

769 [24] Ding X., Suzuki T., Nomura M., et al., A study on zinc isotope 809 [33] Shaik Y. P., Naidu N. K., Yadavalli V. R., et al., The comparison
770 fractionation in a benzo crown resin/acetone system. *Bulletin 810 of the mechanical characteristics of ABS using three different
771 of the Chemical Society of Japan*, **79**(9): 1389–1392, 2006. 811 plastic production techniques. *Open Access Library Journal*,
772 <https://doi.org/10.1246/bcsj.79.1389> 812 **10**(5): 1–18, 2023. <https://doi.org/10.4236/oalib.1110097>

773 [25] Miller M. M., Uranium enrichment and heavy wa- 813 [34] Wang Zhong, Effects of different test conditions on the heat
774 ter production. *Energy*, **9**(9–10): 829–846, 1984. 814 distortion temperature of general-purpose plastics. *Physical
775 [https://doi.org/10.1016/0360-5442\(84\)90014-8](https://doi.org/10.1016/0360-5442(84)90014-8) 815 and Chemical Inspection - Physical Division*, **58**(12): 4–7,
776 [26] Ye J. H., Yu T., Efficient and selective extraction of uranium 816 2022. <https://doi.org/10.11973/lhjy-wl202212002>

777 from seawater based on a novel pulsed liquid chromatography 817 [35] Chen Lei, Liu Peng, Dang Miao, Progress of adsorp-
778 radionuclide separation method. *Nuclear Science and Tech- 818 tion of uranium ions by inorganic minerals*. *Frontiers
779 niques*, **34**(2): 19, 2023. [https://doi.org/10.12677/AEP.2021.113067](https://doi.org/10.1007/s41365-023- 819 of Environmental Protection</i>, 11(03): 604–608, 2021.
780 01180-9 820 <a href=)

781 [27] Palkin V. A., Optimization of a centrifuge cascade for sepa- 821 [36] Chen Renhai, Experimental study on drag reduction of
782 rating a multicomponent mixture of isotopes. *Atomic Energy*, 822 cetyltrimethylammonium chloride. *Harbin Institute of Tech-
783 **115**(2): 109–115, 2013. <a href="https://doi.org/10.1007/s10512-013- 823 nology</i>, 2009.*

784 9757-0